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ISSN 1070-4272, Russian Journal of Applied Chemistry, 2015, Vol. 88, No. 10, pp. 1570−1575. © Pleiades Publishing, Ltd., 2015.
Original Russian Text © A.S. Savenkov, O.N. Bliznjuk, P.V. Kuznetsov, Yu.L. Vyatkin, N.Yu. Masalitina, 2015, published in Zhurnal Prikladnoi Khimii, 2015, Vol. 88, No. 10, pp. 1384−1389.

INORGANIC SYNTHESIS AND INDUSTRIAL INORGANIC CHEMISTRY

Modeling of Ammonia Oxidation on a Platinoid Catalyst, Taking into Account the N_2O Formation

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Received December 21, 2014

Abstract—A mathematical model of ammonia oxidation on a platinoid catalyst, taking into account the N_2O formation, was developed. The possibilities of lowering the amount of N_2O, which is formed as by-product in high-temperature oxidation of ammonia in nitric acid production, are examined. The developed model allows calculation of the reactor for ammonia oxidation using platinoid catalysts of different geometric profiles.

DOI: 10.1134/S107042721510002X

Today the only commercial procedure for nitric acid production is catalytic oxidation of ammonia with atmospheric oxygen, followed by absorption of nitrogen oxides formed in the processes with water. The NH_3 conversion step largely determines the parameters of the whole processes of nitrogen acid production, and the consumption coefficients with respect to NH_3, input and loss of platinum group metals (PGM), and energy characteristics of the flowsheets largely depend on how properly this step is performed.

The studies performed by now [1–4] substantiate the suggested mechanism of the catalytic oxidation of ammonia on platinoid gauzes, suggest a kinetic model of the process, and allow finding the conditions that ensure the maximal NO yield. The results of our experimental studies on NH_3 oxidation on platinoid catalysts in combination with the published data show that, to ensure the maximal selectivity with respect to NO and the high intensity of the process, it is necessary to maintain conditions at which the overall process is controlled by external diffusion. At low NH_3 concentrations on the catalyst surface, typical of external diffusion control, the rate of NH_3 oxidation to N_2O and N_2 sharply decreases, and it undergoes selective oxidation to NO [1–4].

One of the drawbacks of the previous studies and developed models is the lack of data on the formation of N_2O, which is formed as by-product of catalytic oxidation of NH_3 in the course of HNO_3 production [5–7]. Dinitrogen monoxide passes through all the remaining steps of the HNO_3 technology without changes and is discharged into the atmosphere. Nitric acid production facilities in CIS countries discharge today from 6.0 to 7.5 kg of N_2O annually per ton of HNO_3. Recent studies show that N_2O is a strong greenhouse gas whose potential for global warming is 310 times higher than that of CO_2 [8].

To develop a mathematical model of ammonia oxidation to NO taking into account the formation of N_2 and N_2O, we performed a complex of physicochemical, kinetic, and technological studies.

Some of the results of studies on determining the degree of ammonia oxidation to nitrogen monoxide NO and dinitrogen monoxide N_2O, obtained in a flow-through installation, are given in Tables 1 and 2. As catalyst we took industrial knitted gauzes of the following composition, %: Pt 90, Rh 10; $d_w = 0.07 \times 10^{-3}$ m; number of interweavings per 1 m^2 of the gauze 1024; wire surface area 1.407 m^2 m^{-2} gauze.

Tables 1 and 2 show that the oxidation to NO even at the maximal NO yield is accompanied by concurrent oxidation of ammonia to N_2O and N_2, although the rates of these processes are low. Simultaneously, the transformation of NO into N_2 was revealed. Similar data

Table 1. Yield of nitrogen monoxide α in relation to the contact time and linear velocity. P = 0.45 MPa, T = 1123 K, c_{NH_3} = 10–11 vol %

ω, m s^{-1}	Yield α, %, at indicated contact time τ × 10^4, s						
	0.27	0.54	1.08	1.62	2.0	3.0	5.0
0.5	64.0	71.5	86.8	95.4	94.8	94.3	93.4
1.0	68.2	79.8	91.4	95.8	95.2	94.6	93.6
2.0	74.5	87.0	96.0	96.2	95.6	95.0	93.9
4.0	83.3	94.2	96.1	96.0	95.8	95.2	94.0
6.0	89.0	94.4	96.2	96.2	95.8	95.2	94.0
8.0	89.9	94.3	96.1	96.1	95.8	95.2	94.0

were obtained on woven platinum gauzes with the wire diameter $d_w = 0.092 \times 10^{-3}$ m. The experimental results show that the degrees of conversion of ammonia into NO and N_2O on the knitted and woven gauzes are very similar.

The stoichiometric basis of the pathways of ammonia oxidation, taking into account the formation of dinitrogen monoxide, for the platinoid catalyst is the following:

$$4NH_3 + 5O_2 \xrightarrow{k_1} 4NO + 6H_2O, \quad (1)$$

$$4NH_3 + 4O_2 \xrightarrow{k_2} 2N_2O + 6H_2O, \quad (2)$$

$$4NH_3 + 3O_2 \xrightarrow{k_3} 2N_2 + 6H_2O, \quad (3)$$

$$2NO \xrightarrow{k_4} N_2 + O_2. \quad (4)$$

The modeling consists in obtaining a mathematical description of the process in the catalyst bed, taking into account the transfer processes on the basis of the reaction mechanism concepts. Oxygen occurs on the platinum surface at high temperatures in the dissociated state. On the free catalyst surface, ammonia undergoes adsorption, dissociation, and formation of intermediates, which react with each other to form NO, N_2O, N_2, and H_2O and leave the catalyst surface at 973–1193 K (Table 3).

In the course of catalysis, ammonia acts as electron donor, and oxygen, as electron acceptor. When being adsorbed, O_2 molecules add electrons donated by the catalyst and transform into surface oxygen atoms (step 1). In step 2, the NH_3 molecule donates electrons to the catalyst surface that is not covered with oxygen, the N–H bonds in it become weaker, and imide-type species are formed. On the catalyst surface that is covered with oxygen, ammonia forms imide-type species (step 3), which subsequently recombine to form nitrogen (step 7). The subsequent addition of oxygen to the imide (steps 4, 5) leads to the formation of NO. Steps 6, 8, and 9 are associated with the formation of N_2O, N_2, and H_2O.

The suggested detailed mechanism of the process was used for deriving the rate equations describing the reactions occurring on the catalyst surface with the formation of NO, N_2O, and N_2.

Excluding the concentrations of the intermediates, we obtain a kinetic model of the process in the form of the system of rate equations for separate steps. The rates along pathways I–IV are described by the expressions

Table 2. Yield of dinitrogen monoxide α in relation to the pressure and contact time. T = 1123 K, ω = 2 m s^{-1}

τ × 10^4, s	Yield α, %, at indicated P, MPa			
	0.1	0.45	0.73	1.1
0.54	0.6	1.3	2.76	4.5
1.08	0.5	0.85	1.47	2.3
2.0	0.4	0.7	1.3	2.1

$$r_1 = k_1 P_{NH_3} P_{O_2}^{0.5}, \quad (5)$$

$$r_2 = k_1 P_{NH_3} P_{O_2}, \quad (6)$$

$$r_3 = k_3 P_{NH_3}, \quad (7)$$

$$r_4 = k_4 P_{NO}^2, \quad (8)$$

where k_1, k_2, k_3, and k_4 are the rate constants for the corresponding pathways.

For the reaction involving the consumption of ammonia and formation of NO, we obtain

$$r_{HN_3} = -k_1 P_{NH_3} P_{O_2}^{0.5} - k_2 P_{NH_3} P_{O_2} - k_3 P_{NH_3}, \quad (9)$$

$$r_{NO} = k_1 P_{NH_3} P_{O_2}^{0.5} - k_4 P_{NO}^2. \quad (10)$$

Equations (5)–(10) were used for describing the ammonia oxidation on platinoid gauzes.

The process occurring in the catalyst bed under the conditions of external diffusion control is characterized by high temperature gradient. At a small height, several centimeters over the catalyst, the gas undergoes heating to the value of the adiabatic heating of the reaction mixture from 473 to 1173 K. This can lead to considerable longitudinal transfer of the heat and substance. However, the effective coefficients of longitudinal diffusion and thermal conductivity of the gas phase are low, and the longitudinal heat transfer mainly occurs through the solid skeleton of the catalyst bed. To describe the process, it is admissible to neglect the effect of flows arising in the nonisothermal boundary layer of a multicomponent mixture: Stefan flow, thermal diffusion, and diffusion thermal conductivity, because the reaction mixture volume changes by no more than 10%, the mixture is strongly diluted with an inert gas (N_2), and the molecular masses of the components and, correspondingly, their diffusion coefficients differ insignificantly [7]. The catalyst temperature in a bed of platinoid gauzes is assumed to be constant and is determined by the value of the adiabatic heating of the feed. Therefore, to describe the process, we assume the plug-flow model for the gas phase, using the material balance equations for each component.

The material balance equation for the process occurring with significant effect of the external mass transfer has the following form for ith component:

$$\frac{d(V_0 c_i)}{dV_{kat}} = \beta_i (c_i - c_{i,s}) S_{sp}, \quad \text{at } V_{kat} = 0 \;\; V_0 c_i = V_0 c_{0i}, \quad (11)$$

where the components i = 1, 2, 3, 4, 5, and 6 are NH_3, O_2, NO, H_2O, N_2O, and N_2, respectively; $V_0 c_i$, molar amount of ith component in the catalyst bed (mole); V_{kat}, catalyst bed volume (m^3); c_i, $c_{i,s}$, running concentration of ith component in the reactant flow and on the surface, respectively (mol m^{-3}); c_{0i}, initial concentration of ammonia and oxygen in the reaction mixture (mol m^{-3}); β, mass exchange coefficient between the catalyst surface and reaction mixture flow (m s^{-1}); S_{sp}, geometric specific surface area of the platinoid catalyst per unit volume (m^2 m^{-3}).

Table 3. Assumed mechanism in elementary steps[a]

Step no.	Step	I	II	III	IV
1	O_2 + 2kt ↔ 2ktO	5/4	4/4	3/4	–1
2	NH_3 + 3kt ↔ ktNH +2ktH	1	1	1	0
3	NH_3 + ktO → ktNH + H_2O	1	1	1	0
4	ktNH + ktO → ktNO + ktH	1	0	0	0
5	ktNO → NO+ kt	1	0	0	2
6	kt + NH + ktNO → N_2O + ktH	0	1/2	0	0
7	2ktNH → N_2 + 2ktH	1/2	0	1/2	0
8	2ktH + ktO → H_2O + kt	3/2	3/2	3/2	0
9	2ktNO → N_2 + 2ktO	0	0	0	1

[a] (kt) Free site on the catalyst surface and (I–IV) stoichiometric numbers of the corresponding pathway.

After transforming Eq. (11) for ammonia and oxygen, we obtain

$$\frac{dx_i}{d\tau} = \frac{\beta_i S_{sp}}{10^4 y_{0i}}(y_i - y_{is}), \quad (12)$$

where $i = 1, 2$; x_i is the degree of conversion of ammonia and oxygen (fractions of unity); y_{0i}, initial mole fraction of ammonia in the mixture; y_i, y_{is}, running mole fraction of ammonia and oxygen in the volume and on the catalyst surface; τ, contact time (s); $\tau = V_{kat}/V_0$; V_0, flow rate of the gas mixture under normal conditions ($T = 273$ K, $P = 1.013 \times 10^5$ Pa) ($m^3\ s^{-1}$).

Similar equations were obtained for all the components of the reaction mixture. The mathematical description of the ammonia oxidation in the catalyst bed is as follows:

$$\frac{dx_k}{d\tau} = \frac{\beta_k S_{sp}}{10^4 y_{01}}(y_k - y_{ks}). \quad (13)$$

Boundary conditions: $\tau = 0$, $x_i = 0$, $x_k = 0$, where $k = 3, 4, 5, 6$; x_k is the number of moles of NO, H_2O, N_2O, and N_2, formed from 1 mol of ammonia.

The mole fraction of nitrogen, y_6, was calculated by the equation

$$y_6 = 1 - \sum_{i=1}^{5} y_i. \quad (14)$$

The running concentration of the components in the mixture on the mole fraction scale was calculated by the formula

$$y_i = \frac{y_{0i}(1-x)}{N}, \quad (15)$$

where $i = 1, 2$.

$$y_k = \frac{y_{0i} x_k}{N}, \quad (16)$$

where $k = 3, 4, 5, 6$; N is the running number of moles of the reaction mixture, equal to the sum of the running number of moles of each component.

The substance concentrations on the catalyst surface were determined from the following system of equations:

$$\frac{\beta_i P}{RT}(y_i - y_{s,i}) = \sum_{j=1}^{4} \nu_{ij} r_j, \quad (17)$$

$$K(T_s - T_0) = \sum_{j=1}^{4} \Delta H_j r_j, \quad (18)$$

$$y_{6s} = 1 - \sum_{i=1}^{5} y_{is}, \quad T_s = \text{const}, \quad (19)$$

where $i = 1, 2, 3, 4, 5, 6$; T_0 is the mixture temperature in the gas volume (K); T_s, temperature of the catalyst surface (K); r_j, reaction rate along jth pathway [reactions (1)–(4)]; ΔH_j, thermal effect of the reaction along jth pathway ($J\ mol^{-1}$); and K, coefficient of heat transfer from the gauzes to the gas flow ($W\ m^2\ K^{-1}$).

The system of Eqs. (12)–(19) is the mathematical model of ammonia oxidation on the platinoid catalyst, controlled by external diffusion.

Using the developed mathematical model, we calculated the degree of oxidation on platinoid catalysts. To calculate the process, it is necessary to know the coefficients of mass and heat transfer from the gas flow to the catalyst, and also the physicochemical properties of the mixture depending on the temperature, pressure, and mixture composition.

The physicochemical properties of the gas mixture components were determined by the following formulas [9–11]:

$$\mathrm{Nu} = \frac{\alpha d_w}{\lambda_m} = a + b\,\mathrm{Re}^{0.6}\,\mathrm{Pr}^{0.38}, \quad (20)$$

$$\mathrm{Sh}_i = \frac{\beta_i d_w}{D_i} = a + b\,\mathrm{Re}^{0.6}\,\mathrm{Sc}^{0.38}, \quad (21)$$

$$\mathrm{Sc}_i = \frac{\nu_m}{D_i}, \quad (22)$$

$$\mathrm{Pr} = \frac{\nu_m c_{p_m}}{\lambda_{см}}, \quad (23)$$

$$\mathrm{Re} = \frac{\omega \rho_m d_w}{\mu_m}, \quad (24)$$

where d_w is the diameter of the wire in the catalyst gauzes (m); α, heat transfer coefficient ($W\ m^{-2}\ K^{-1}$); λ, thermal conductivity coefficient ($W\ m^{-1}\ K$); μ_m, dynamic viscosity coefficient of the mixture (Pa s); ν_m, kinematic viscosity coefficient of the mixture ($m^2\ s^{-1}$); D_i, diffusion coefficient of ith component in a mixture with other components; a, b, coefficients: $a = 0.273$, $b = 0.246$; ρ, gas mixture density ($kg\ m^{-3}$); and ω, linear velocity of the gas flow ($m\ s^{-1}$).

Using the reference data [11], we determined the parameters μ, ν, ρ, D, and β for each component of the gas mixture.

By solving the inverse problem of chemical kinetics, using the experimental data obtained, we found the rate

Table 4. Results of calculating the degree of conversion using the developed model (P = 0.45 MPa)

Component	Initial concentration, fraction of unity	Conversion, %, at indicated contact time $\tau \times 10^4$, s				
		1	2	3	4	5
T = 1123 K, ω = 2 m s^{-1}, knitted gauzes, d_w = 0.07 × 10^{-3} m						
NH_3	0.1	94.39	99.672	99.981	99.999	100.00
O_2	0.2	60.1210	61.8609	61.7056	61.4859	61.2659
NO	0.0001	95.1486	96.3754	95.5884	94.7038	93.8236
H_2O	0.015	96.7352	99.8856	99.9960	99.999	100.00
N_2	0.684	22.1716	23.3283	23.7997	24.2432	24.6817
N_2O	0.0001	0.8327	0.7397	0.6400	0.5400	0.4400
T = 1173 , ω = 2 m s^{-1}, knitted gauzes, d_w = 0.07 × 10^{-3} m						
NH_3	0.1	94.39	99.672	99.981	99.999	100.00
O_2	0.2	60.7988	62.0356	61.8937	61.7190	61.5446
NO	0.0001	96.4711	97.0145	96.3628	95.6617	94.9643
H_2O	0.015	97.6765	99.9425	99.9986	100.00	100.00
N_2	0.684	22.3356	23.2000	23.5650	23.9152	24.2626
N_2O	0.0001	0.6095	0.5141	0.4442	0.3242	0.2142
T = 1073 K, ω = 2 m s^{-1}, knitted gauzes, d_w = 0.07 × 10^{-3} m						
NH_3	0.1	94.39	99.672	99.981	99.999	100.00
O_2	0.2	59.4333	61.5221	61.4063	61.2006	60.9929
NO	0.0001	93.2966	95.0854	94.3907	93.5583	92.7272
H_2O	0.015	96.1341	99.8352	99.9933	99.997	100.00
N_2	0.684	22.5239	23.7942	24.2508	24.6701	25.0843
N_2O	0.0001	0.9356	0.8240	0.7244	0.6444	0.5424
T = 1073 K, ω = 2 m s^{-1}, woven gauzes, d_w = 0.092 × 10^{-3} m						
NH_3	0.1	94.3232	99.632	99.961	99.999	100.00
O_2	0.2	59.4433	61.534	61.3163	61.3106	60.7939
NO	0.0001	93.3466	94.9864	94.2991	93.6573	92.5276
H_2O	0.015	96.2351	99.6652	99.8953	99.996	100.00
N_2	0.684	22.4259	23.6841	24.3548	24.5711	25.1833
N_2O	0.0001	0.9256	0.8142	0.7046	0.6341	0.5321

constants of the ammonia oxidation reactions yielding NO (k_1), N_2O (k_2), and N_2 (k_3), the rate constant of formation of molecular nitrogen N_2 via decomposition of nitrogen monoxide (k_4), and the substance concentrations on the catalyst surface. The results of calculating the degrees of conversion for each component are given in Table 4.

The calculated degrees of conversion agree with the experimental data within 1–3%.

CONCLUSIONS

(1) A mathematical model was developed for the NH_3 oxidation, taking into account the physicochemical features of the ammonia–air mixture and nitrogen oxides. The rate constants and their temperature dependences were found. This allows finding the optimum process conditions for oxidation on platinoid catalysts at different pressures in a wide range of variation of process parameters and determining the amount of the formed dinitrogen monoxide N_2O.

(2) A program based on this model was developed for calculating the oxidation reactor with platinoid catalysts of different geometric profiles.

(3) The catalyst surface area and volume change in the course of operation. With this factor taken into account, a version of the mathematical model was developed with the rates of the ammonia oxidation steps related to the unit weight of the platinoid catalyst.

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